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Synthesis and Nonlinear Studies on Selected Organic Compounds in Nanostructured Thin Films

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Abstract

Organic compounds based on ferrocene, pyrazolone, and octahydroacridine exhibit high interest due to their unusual structure, with potential practical applications due to their special optical properties. Nonlinear optical (NLO) properties of some new synthesized derivatives are evaluated in relationship with the chemical structure by using DFT molecular modeling. In condensed state, ferrocene and other organic molecules were found in a staggered arrangement (D5d) as a nonpolar molecule, but the eclipsed (D5h) and twisted (D5) forms exhibit SHG capabilities. The molecular polarizability (α), first-order hyperpolarizabilities (β_{tot}), dipole (μ_{tot}), and quadrupole (Q) moments were computed. The NLO efficiency was assessed by the relationship between high (β_{tot}) and low HOMO-LUMO energy gap. The nonlinear optical properties of some new synthesized compounds were evaluated in thin films with nanometric morphology obtained using various methods: Langmuir-Blodgett (LB) thin films, sol-gel deposition, and layer-by-layer deposition.

Keywords: nonlinear optics, thin films, nanostructures, hybrid materials
Langmuir-Blodgett film, layer by layer

1. Introduction

Nonlinear optics has become a vibrant field of research since the optical second-harmonic generation (SHG) was first observed in the early 1960s [1]. A better understanding was achieved on the origin of nonlinear optical (NLO) phenomena and the structure-property relationships of NLO chromophores in the late 1970s when various tools were developed to accurately measure and calculate hyperpolarizabilities [2]. Organic NLO materials, which can be modulated and processed readily, are of much contemporary interest because of their potential applications in modulation of optical signals, medicine, spectroscopic and

electrochemical sensing, microfabrication and imaging, laser technology, data storage, and telecommunication [3]. Recent studies were focused on the synthesis of the organic molecules with special geometry and certain electronic molecular parameters to possess nonlinear optical (NLO) properties [3–24]. The demand of substances with NLO properties for numerous industrial applications has resulted in many articles reporting the manufacture of various novel molecules, with highly active chromophores and superior optical activity. However, it remains the issue of processing these materials, as long as the specific optical properties have to be preserved, together with new requirements added, such as chemical stability, mechanical strength, etc. The main materials used as host for the embedding of chromophores and fabrication methods are discussed. The influence of parameters (such as chemical structure of the host material, synthesis conditions, and external stimuli) on the optical and electrical properties of the final product is also evidenced.

2. Synthesis of compounds with NLO properties

Recent literature shows some classes of organic compounds suitable for applications for molecular switches that possess certain characteristics, such as high molecular hyperpolarizability coefficients (β), special geometry, and in most cases small HOMO-LUMO energy gaps [25–27]. In the following sections, we will refer to the recent synthesis of several classes of organic compounds possessing the abovementioned characteristics.

2.1. Alkyne compounds

Ryhding et al. synthesized by Sonogashira Pd-catalyzed cross-coupling reactions a series of new oligo(*p*-phenyleneethynylene) **1–4** (Scheme 1) [28]. Miao et al. successfully synthesized a series of novel donor-acceptor chromophores **5–8** in an excellent yield by metal-free [2 + 2] click chemistry. These compounds possessed energy-level modulation of the organic π -conjugated aniline derivatives (see **Figure 1**) [29].

The new derivatives **9–10** were obtained by Michinobu et al. in quantitative yield (96–100%) by [2 + 2] cycloaddition between tetracyanoethylene- and dimethylanilino-substituted alkynes, followed by electrocyclic ring opening of the initially formed cyclobutenes [30].

2.2. Push-pull derivatives as NLO chromophores

The organic molecules which contain a couple, donor (D)-acceptor (A) (or “push-pull” system), connected to a system which contributes to the delocalization of the π -electrons make the *classic structures* with optical response due to large hyperpolarizabilities that arise from a combination of strong electron-donating groups (e.g., —NR_2 , —OR) and strong electron-withdrawing groups (e.g., —NO_2 , —CN), positioned at the opposite ends of a conjugated system (see **Figure 2**) [16, 23, 31, 32]. Therefore, the synthesis of the classic structures occupies a central place even in the current research.

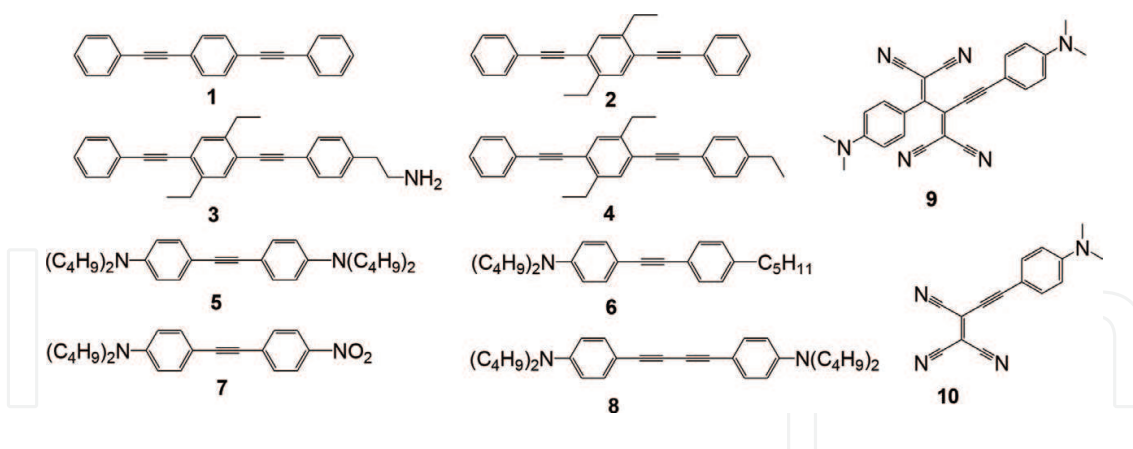


Figure 1. Alkyne compounds with NLO properties [28–30].



Figure 2. Organic structures that contain a couple: donor-acceptor or a “push-pull” system [32].

There are several classes of organic compounds in this category, from which some representatives will be presented.

2.2.1. Push-pull dyes

Arylazo-5-alkoxy-2,2'-bithiophene-conjugated dyes **11**, synthesized through a combination of the Friedel-Crafts and the Lawesson reactions by Raposo et al., have been proven as promising NLO chromophores (see **Figure 2**). Compounds **11** exhibit high molecular nonlinearities, as their values are 13–16 times higher than that of the well-known 4-nitroaniline (PNA) and the corresponding β_0 values are 2.5 to 4 times higher than that of PNA (see **Figure 3**) [33].

Kleinpeter et al. demonstrated that compounds **12** possessed excellent values of molecular hyperpolarizability β_0 ; therefore, they can be considered as candidates for nonlinear optical (NLO) applications [34]. A series of pyrazole-5-ones **13**, synthesized by azo-coupling reactions, which present only hydrazo tautomers with a planar structure, responsible for their nonlinear optical properties were discussed in terms of NLO parameters by Marinescu et al. [32]. Herein, the NLO efficiency of compounds was assessed by the relationship between high β_{tot} and low HOMO-LUMO energy gap. Also, these compounds can function as ligands for erbium complexes, which possessed solvatochromic properties and have NLO material characteristics [35]. Zajac et al. reported that the synthesis of benzothiazole dyes **17** and their NLO properties was investigated [36]. Formulation of 2-heteroaryl-benzothiazoles by Vilsmeier-Haack reaction gives the corresponding carbaldehydes, which subsequently underwent a Wittig reaction providing target compounds in good yields [36].

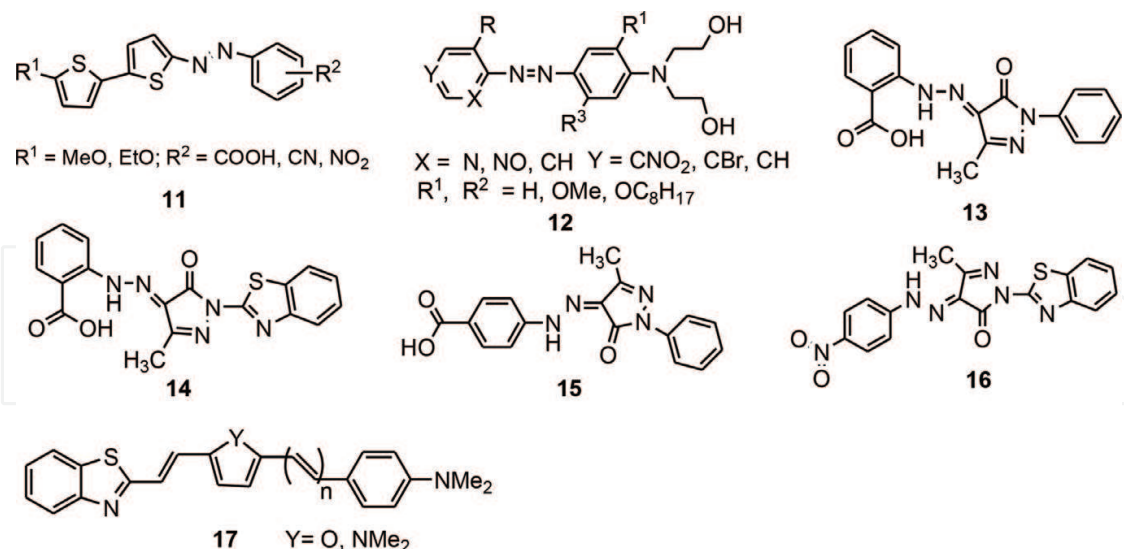


Figure 3. Push-pull dyes as NLO chromophores [33–36].

2.2.2. Push-pull structures from different classes of heterocyclic compounds

Push-pull molecular structures based on angular benzobisthiazolium acceptor were synthesized by Cibova et al. A comparison of selected spectral and nonlinear optical properties of the prepared compounds shows that compound **18** possess the best NLO properties (see **Figure 4**) [37]. Hebbar et al. describe the synthesis of various push-pull molecules **19–20** with a central pyrazine unit connected to a hexatriene chain terminated by various *p*-substituted phenyl groups. The compounds were synthesized by a Negishi coupling reaction followed by Wittig and Wadsworth-Emmons reactions [38]. Cho et al. synthesized new efficient push-pull organic semiconductors comprising of the bis(9,9-dimethyl-9H-fluoren-2-yl)aniline donor and the various acceptors such as NO_2 , 4-dicyanomethylene-6-*tert*-butyl-4H-pyran, and 2-dicyanomethylene-3-cyano-5-dimethyl-2,5-dihydrofuran, which were linked with bithiophene or vinyl bithiophene *p*-conjugation bridges, were synthesized, and their photovoltaic characteristics were investigated in solution-processed small molecule organic solar cells (SMOSCs) [39].

The compounds **21–23** were readily prepared through Knoevenagel condensation reaction with 5-bromo-5'-nitro-2,2'-bithiophene, 2-(2-*tert*-butyl-6-methyl-4H-pyran-4-ylidene) malononitrile, and 2-(3-cyano-4,5,5-trimethyl-5H-furan-2-ylidene)malononitrile, respectively, and a palladium-catalyzed Suzuki coupling reaction with 2-bromo-5-nitrothiophene using phase-transfer catalyst. Shi et al. synthesized boron dipyrromethene **24** derivative bearing an electron-donating 4-(dimethylamino)phenylethynyl group and an electron-withdrawing 4-nitrophenylethynyl group in the opposite two and six positions by Knoevenagel condensation followed by sequential Sonogashira coupling reactions and the second-order nonlinear optical properties of this compound has been studied [40]. Farat et al. synthesized novel xanthene push-pull chromophores and luminophores **25–26** and show these structures as the more pronounced vibrational bands in the luminescence spectra, which indicate the more rigid structure of these molecules in the excited state [41]. Malytskyi et al. synthesized thiophene-based push-pull chromophores **27–28**

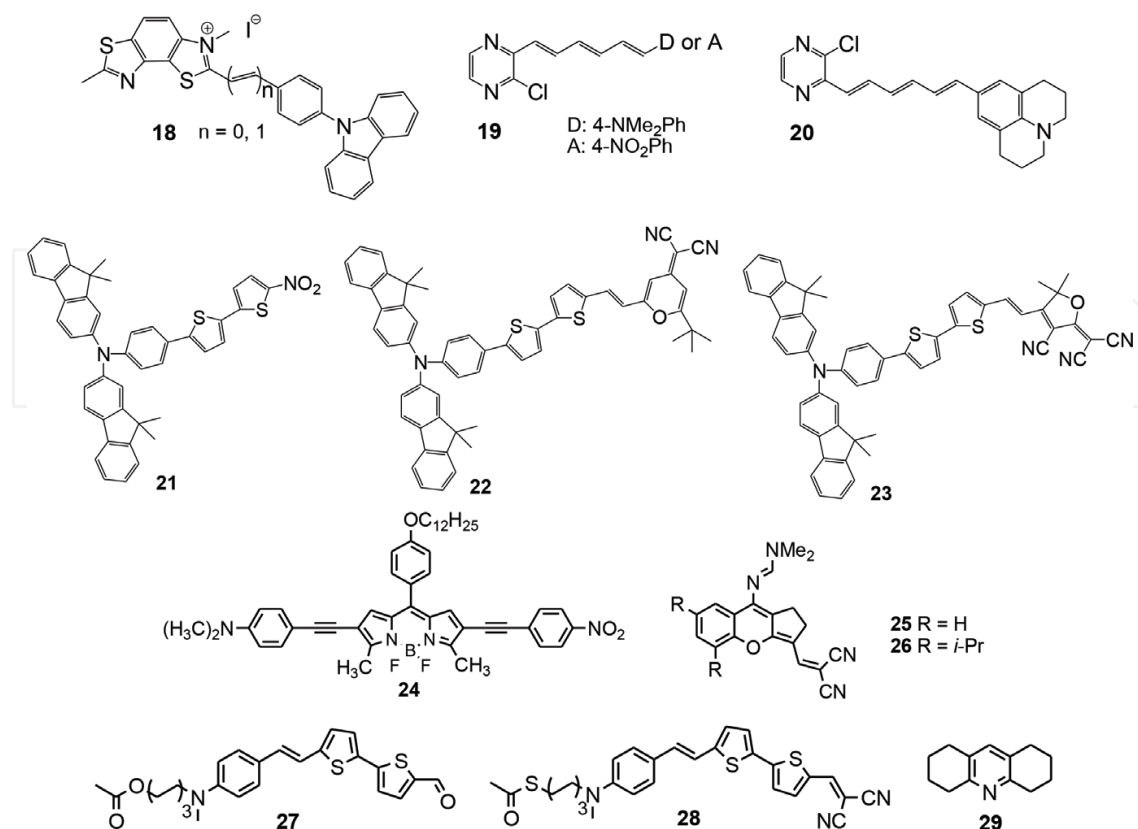


Figure 4. Push-pull molecules as NLO chromophores [37–43].

for tuning the electrical and optical properties of surfaces with controlled self-assembled monolayer (SAM) formation [42]. Ion et al. reported for smooth/compact 1,2,3,4,5,6,7,8-octahydroacridine **29** thin films grown by matrix-assisted pulsed laser evaporation (MAPLE) the presence of the SHG (second-harmonic generation) signal related to the conformational asymmetry of the OHA molecule and therefore the nonlinear optical applications of it [43].

2.3. Thienyl compounds as NLO materials

Thiophenes are among the most studied heterocyclic spacers for D- π -A systems due to their relatively low resonance energies and have allowed the preparation of chromophores with high stabilities and nonlinearities [44]. Raposo et al. reported the synthesis of formyl-substituted 1-alkyl(aryl)-2-(2'-thienyl)pyrroles **30–32** as versatile building blocks for NLO materials, by functionalization of the pyrrole or thiophene ring of thienylpyrroles using different methods: Vilsmeier formylation or metalation followed by reaction with DMF (see **Figure 5**) [45]. Batista et al. reported the synthesis of new chromophores with second-order nonlinearities containing thienylpyrrolyl and benzothiazolyl moieties. The solvatochromic behavior of the compounds was investigated, and the hyperpolarizabilities β of derivatives **33–35** were measured using hyper-Rayleigh scattering [46]. A series of thienylpyrrolyl π -conjugated systems attached to functionalized benzimidazole heterocycles **36–37** were developed by Batista et al. [47]. These chromophores possess excellent solvatochromic properties and good molecular optical nonlinearities. Herbivo et al. reported the synthesis of a series of formyl-substituted

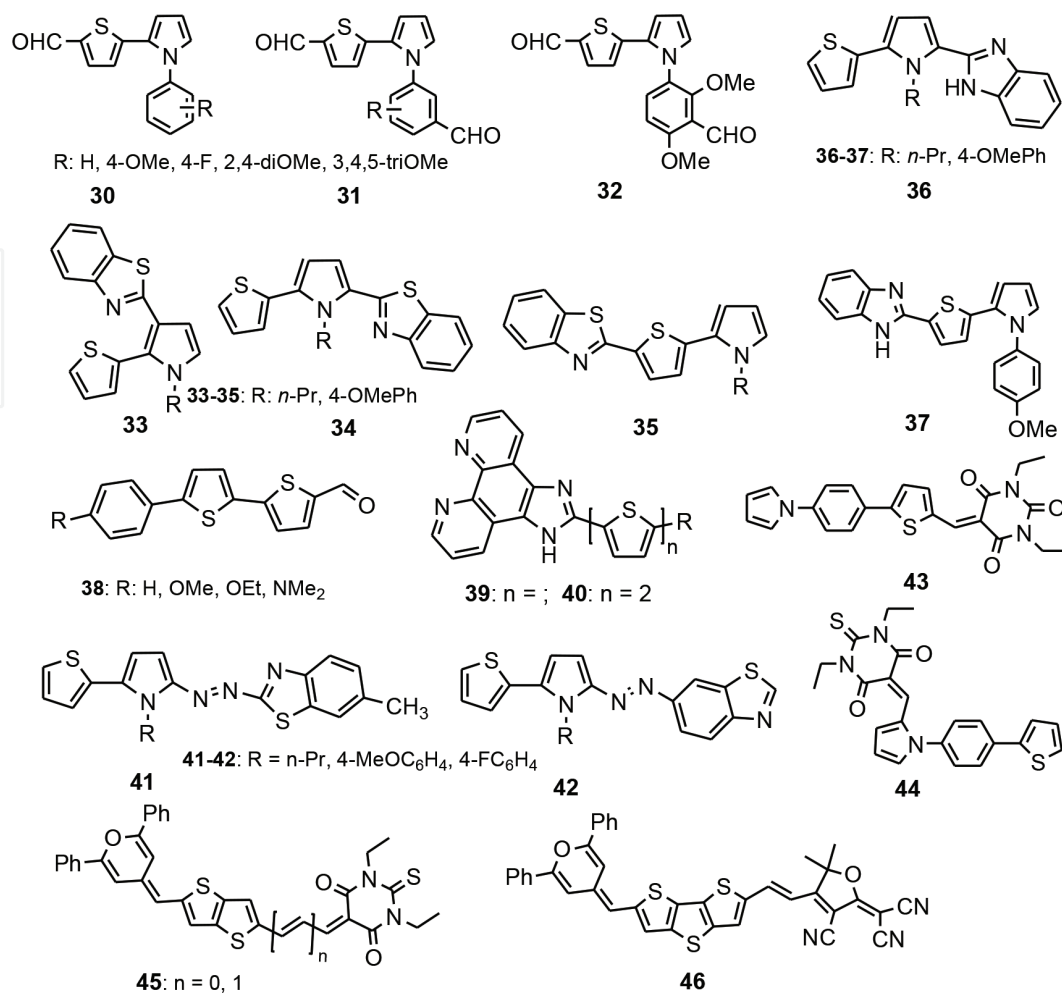


Figure 5. Structures of thienyl compounds with nonlinear optical properties [44–51].

5-aryl-2,2'-bithiophenes **38** using two different methods: Vilsmeier-Haack-Arnold reaction and through Suzuki coupling as precursors for NLO materials [48]. Batista et al. synthesized that chromophores possess an (oligo)thienyl *p*-conjugated system attached to an imidazo-phenanthroline moiety by condensation of phenanthroline-5,6-dione with formyl-thiophene derivatives in the presence of ammonium acetate in glacial acetic acid. Compounds **39–40** possess good values of β hyperpolarizabilities and solvatochromic properties [49]. Raposo et al. reported the synthesis of the two series of donor-acceptor conjugated heterocyclic azo-thienylpyrrole system **41–42**. The compounds **41** have the largest first-order hyperpolarizabilities ($\beta = 460\text{--}660 \times 10^{-30}$ esu, T convention) [50]. Castro et al. designed two series of novel push-pull 1-(4-(thiophen-2-yl)phenyl)-1H-pyrroles **43–44** to explore the consequence of using different electron-accepting moieties linked to the thiophene at the arylthiophene bridge or to the pyrrole heterocycle, which plays the role of donor group. Thiobarbituric acid derivative **5b** functionalized in the thiophene ring exhibits the largest first-order hyperpolarizability ($\beta = 2480 \times 10^{-30}$ esu) [51]. Marco et al. synthesized two series of compounds bearing dithienothiophene or thienothiophene as π -conjugated spacer **45–46** with high second-order molecular nonlinearity [44].

2.4. Ferrocene derivatives

Ferrocene (**47**), or *bis*-cyclopentadienyl iron, is a sandwich-like compound known since 1951 when Pauson and Kealy reacted cyclopentadienyl magnesium bromide with anhydrous ferric chloride (see **Figure 6**) [52, 53]. Ferrocene, in bulk or as thin films, is one of the most studied metallocenes. Ferrocene found itself applications not only in a multitude of areas, from chemical synthesis and engineering, e.g., materials chemistry (catalyst in carbon nanotechnology, precursor material, ligand and scaffolding, fuel additives, etc.), and pharmaceuticals (anticancer and other drugs), but also in theoretical and basic research [54–57]. Matei et al. present results on the morphology and optical properties of ferrocene thin films grown by a nonconventional laser-assisted technique, films that were further used in two-photon absorption investigations, evidencing that the compound has low-to-medium SHG capabilities [58]. Constantinescu et al. studied nonlinear optical applications of ferrocene carboxaldehyde **48** thin films grown by matrix-assisted pulsed laser evaporation (MAPLE) [59]. Two-photon absorption investigations reveal that the ferrocene carboxaldehyde thin films deposited by MAPLE have second-harmonic generation capabilities improved compared to simple ferrocene, opening the path toward applications in optoelectronics.

Yang et al. synthesized two electron-donating π -acceptor (D- π -A) chromospheres **49–50**, with ferrocene as the electron donor and pyridinium as the electron acceptor, and investigated the nonlinear optical absorption (NOA) properties in the solution state by the Z-scan technique [60].

Both compounds exhibited reverse saturable absorption (RSA) and optical limiting effect under nanosecond pulse irradiation. Matei et al. synthesized 4-(ferrocenylmethylimino)-2-hydroxy-benzoic **51** acid using a Schiff reaction and deposited thin films of it with controlled thickness by matrix-assisted pulsed laser evaporation (MAPLE), on quartz and silicon substrates, with the aim of evaluating the nonlinear optical properties for potential optoelectronic applications. Second-harmonic generation signals were weak due to the relatively short time of

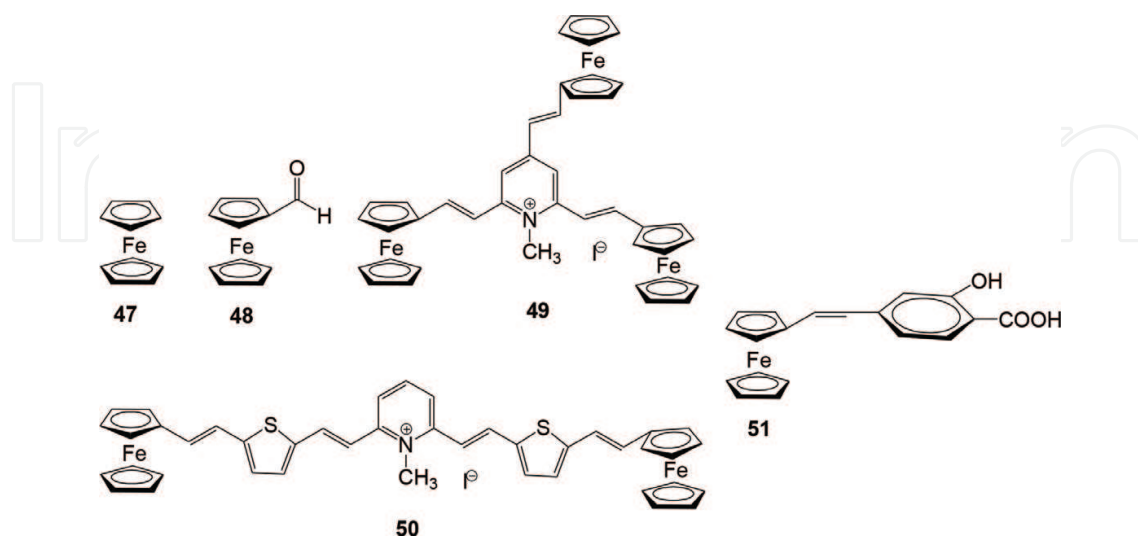


Figure 6. Ferrocene derivatives with nonlinear optical properties [52–60].

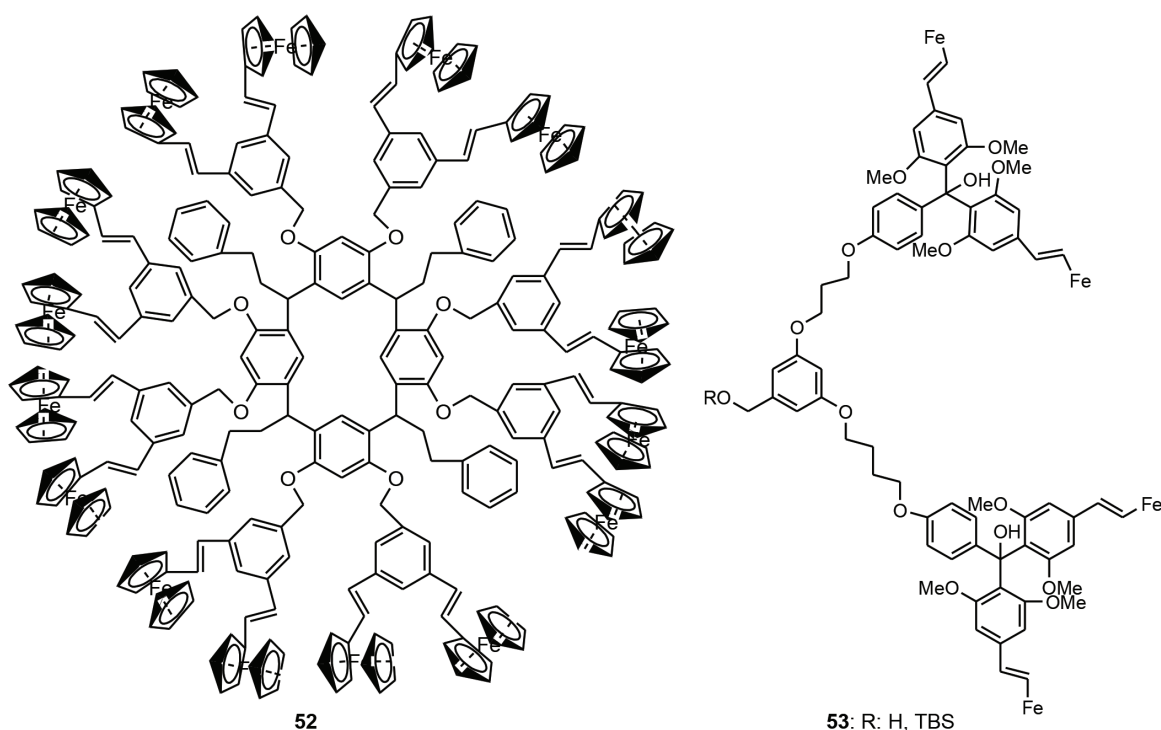


Figure 7. Ferrocene dendrimers with nonlinear optical properties [62, 63].

recording [61]. Lijanová et al. synthesized dendrimers **52** with ferrocenyl-ended groups joined by vinyl moieties (see **Figure 7**) [62].

The synthesis of the dendrimers with vinyl ferrocene was carried out applying the convergent Frechet approach that consists of three steps: (1) the synthesis of the two conjugated dendrons, (2) the selective formation of resorcinarenes bearing three different solubilizing groups, and (3) the alkylation of the dendrons to the resorcinarenes. Under this order, dendrons containing ferrocenylvinyl groups were prepared starting from a Heck reaction coupling of 3,5-dibromobenzaldehyde with vinyl ferrocene in dimethylformamide/triethylamine (1:0.25) using palladium acetate as catalyst. The $\chi^{(3)}$ values estimated from the THG Maker fringe technique for ferrocenyl-ended resorcinarene dendrimers dispersed in thin solid films are of the order of 10^{-12} esu.

Villalonga-Barber et al. synthesized new dodecaferrocenyl dendrimer **53** using sixfold Huisgen cycloaddition. Each dendron containing four ferrocenyl groups has been synthesized by conventional synthetic methods in good yields [63]. The cyclic voltammetry studies revealed that they all undergo a reversible single-electron transfer process. The absorptions at around 450 nm for the ferrocene-containing carbinols **52** are due to ferrocene d-d bands.

3. Fabrication of thin films with NLO properties

For most practical uses, substances with NLO properties are incorporated into a host material to ensure good dispersibility and stability. Thus, in most of the cases, polymers are used,

usually with electrical and optical properties to improve the performance of the hybrid system. The polymeric derivatives applicable as matrices are the ones with high thermal stability and optical transparency. A large variety of polymers were tested as host matrix, such as polymethyl methacrylates, polyether ketones, polyimides, and polycarbonates. The most used material is polymethyl methacrylate, due to its intrinsic optical properties, stability, functionalization possibilities, and processability. Another material used as the host for NLO substances is silica matrix, which has important advantages: the facility and flexibility of syntheses as well as the possibility of processing them as thin films. Ji et al. [64, 65] report the successful embedding of Disperse Red 1 as chromophore in a silica glass prepared by using sol-gel synthesis. The silicate precursor was a new derivative 1,4 phenylene bis(4-trimethoxysilyl ethyl benzoate), with a structure that allows uniform dispersion and accommodates the chromophore molecules in the cross-linked polymeric matrix (see **Figure 8**).

The hybrid film is fabricated by in situ poling and sol-gel synthesis. The final material exhibits an efficient NLO behavior, with a very good thermal stability (the SHG signal is stable until 120°C, and the half decay temperature is 170°C).

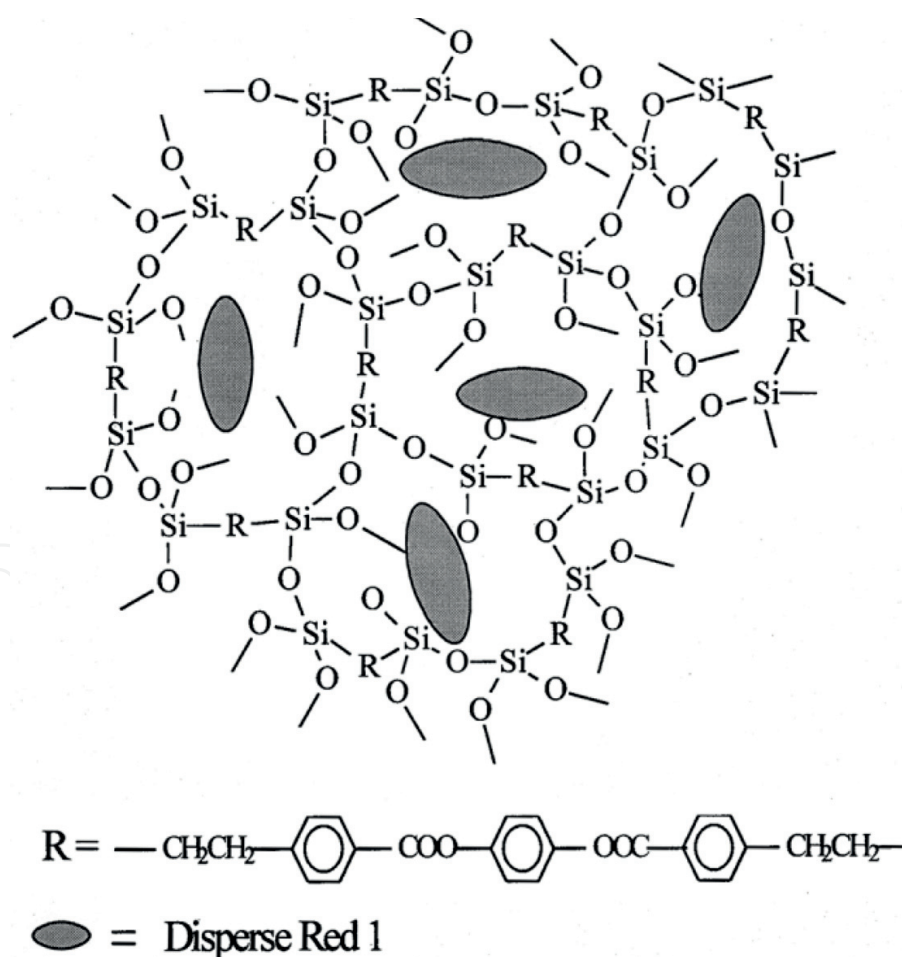


Figure 8. Schematic representation of the silica-based cross-linked film with chromophore Disperse Red 1 (adapted with the permission from reference [64]).

Another advantage of silica as host material is the possibility to prepare polymer-silica hybrid matrix that combines the best properties from both substances. An interpenetrating polymer-silica matrix was prepared [66] from polymerization of γ -methacrylpropyl)-silsesquioxane and an allyl glycidyl ether modified chromophore (Disperse Orange 3 (DO3)). The high degree of cross-link density and order leads to enhancement of the nonresonant second-order nonlinearity in the film obtained. Unfortunately, the process is very difficult and laborious, since the incorporation of the NLO chromophore in the polymer-silica network is a three-step synthesis: (i) functionalization of DO3 with glycidyl ether, (ii) synthesis of monomer (γ -methacrylpropyl)-silsesquioxane using hydrolytic condensation of commercially available silane derivative, and (iii) the preparation of NLO embedded matrix through the free radical polymerization of modified chromophore and methacrylpropyl compound and the simultaneous cross-linking of the network [66].

The AFM images of the DO3-doped methacrylate-silica film before and after poling demonstrate that the poling process allows a better orientational order of the chromophore molecules (see **Figure 9**).

This material exhibits a very good temporal stability of the chromophore orientation in the interpenetrated hybrid polymer-silica matrix, together with superior NLO properties.

Silica material mentioned above could also provide the sites to adjust covalent bonding of the chromophores. Recently, Laskowska et al. [67] reported the fabrication of NLO thin films from a novel functionalized mesoporous silica material as host matrix. To show the efficiency of the concept in tuning the NLO behavior from the morphology of the silica matrix, a very simple optically active compound is proposed, a dipolar copper propyl phosphonate fragment. The copper-containing functional groups are covalently linked to the silica wall inside the pore of the matrix. The structure of the proposed material is presented schematically in **Figure 10**.

The host matrix consists in mesoporous silica thin films with 2D hexagonally distributed nanometric pores. The suitable morphological characteristics of the silica material, with

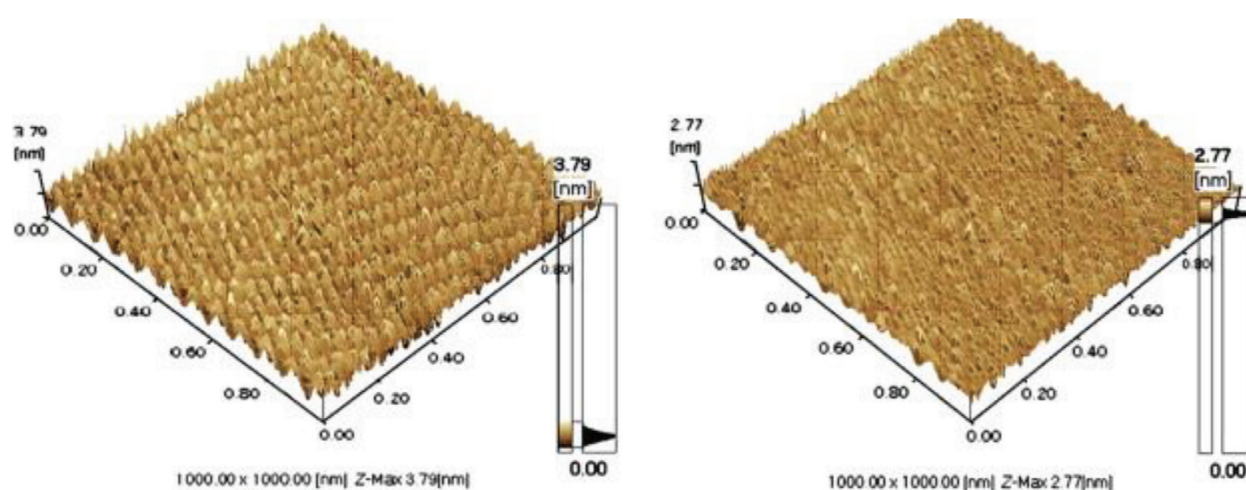


Figure 9. The AFM images of the film before and after poling 2 h at 150°C (reproduced with permission from reference [66]).

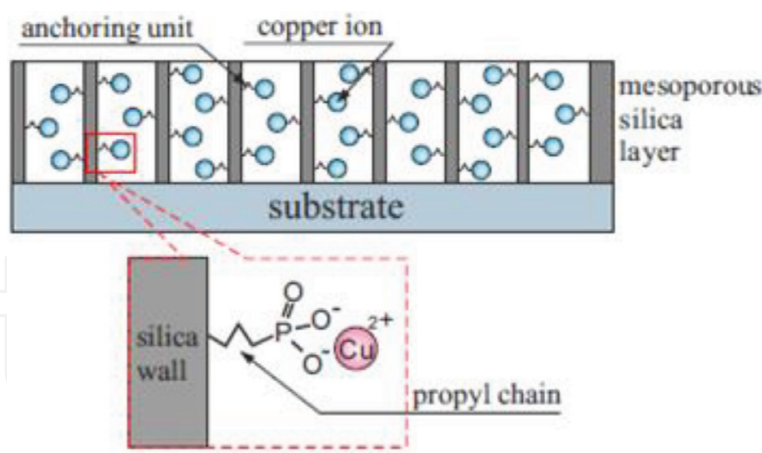


Figure 10. Schematic representation of the structure of mesoporous silica thin layer with Cu^{2+} propyl phosphonate chromophore bonded into pores (adapted with the permission from reference [67]).

hexagonal pores, regularly 2D distributed and aligned perpendicularly to the substrate, provide large specific area for easy access to the pore interior and lead to a high loading of the active chromophore. Moreover, the optical active moieties are very uniformly distributed.

Since the SHG signal obtained depends on the concentration of the NLO fragments, the material with tunable NLO response could be obtained by adjusting the functionalization degree from the synthesis parameters.

4. The arrangement of chromophores in polymeric host matrix

The macromolecular host matrix encapsulates the chromophores either dispersed or attached on the polymeric chain. In both cases, the most important issue that appears is the proper arrangement of NLO active molecules. The common procedure to obtain the required noncentrosymmetric arrangement for the dipolar push-pull chromophores embedded in a polymeric matrix is based on electric field poling process. It consists in the application of the electric field across the material, when heating the system to the glass transition temperature (T_g) of the polymer.

When photosensitive dyes are encapsulated, for example, azo-derivatives, light can be used in order to replace the heating procedure (photoassisted poling). This method is a choice when temperature-sensitive NLO molecules are involved, enabling poling process preformed at temperatures well below T_g . A large variety of azo-derivatives have been poled using this method (1).

Other guest molecules may be covalently bonded to the polymer chain, but the chemistry involved in the attachment of the chromophore to the macromolecule still remains a major challenge. Severe conditions in synthesis and processing employed to prepare most of side-chain NLO polymers (polymers with grafted chromophore as side chain) limit their practical application. The use of these polymer-based materials generates several film properties

required for photonic applications, such as thermal and chemical stability, high loading of the active molecule, and stability of the chromophore orientation [68]. Highly cross-linking of side-chain polymers enhances the stability of the thin film together with the chromophore moiety arrangement.

Another covalent bonded variant is main-chain NLO polymer, with chromophores linked in the backbone at either end of the chromophore or linked at both ends of the chromophores, to form the polymer backbone. The dye fragment can be processed in various configurations: a head-to-tail (isoregic), head-to-head (syndioregic), or in random head-to-tail and head-to-head configurations (aregic) (2) [69].

4.1. Langmuir-Blodgett films

The most efficient way to obtain the arrangement of the large dye molecules is to take advantage from their intrinsic self-assembling ability. Hydrophobically modified chemicals that exhibit NLO properties can be efficiently organized as 2D structure using the Langmuir-Blodgett technique. Formation of the coherent and stable Langmuir film at liquid-air interface is mandatory for the further step, the transfer on solid substrate. The self-assembling properties of the NLO compounds could be tuned by chemical modification of the chromophore with various groups with suitable hydrophobicity, but the chemical modification will also influence the optical properties.

Tang et al. [70] report a study on the influence of the terminal group of the modified amphiphilic azobenzene chromophore on the Langmuir-Blodgett monolayer and multilayer formation. The azobenzene NLO derivative was modified with various electron acceptor groups (acetyl, nitro, and cyano), and the self-assembling behavior of the resulted compounds was investigated, to produce monolayers and multilayers deposited onto hydrophobically treated quartz substrate.

The experimental data confirm the molecular modeling conclusion that the packing of modified azobenzene molecules at the water-air interface and the transfer of the film are both due to the equilibrium of non-covalent interactions in the aggregates, dipole-dipole and π - π stacking interactions, respectively. The packing density and the electronic coupling vary strongly with the chemical structure of the functional group (see **Figure 11**).

The possibility to control the internal morphology and stability of the film through the balance of non-covalent interactions leads to the preparation of highly ordered multilayered film with large second-order susceptibility.

Most of the NLO chromophores could not be chemically modified to achieve suitable properties for spreading as Langmuir monolayers at the air-liquid or liquid-liquid interfaces; thus, the formation of Langmuir-Blodgett film is restricted to compound with a required degree of amphiphilicity. At the same time, many NLO materials processed by using Langmuir-Blodgett technique exhibit poor mechanical stability and limited surface area for deposition. A more sophisticated method to ensure the orientation of the chromophore molecules in the polymeric host network is to produce self-assembled thin film with the aid of film-forming matrix.

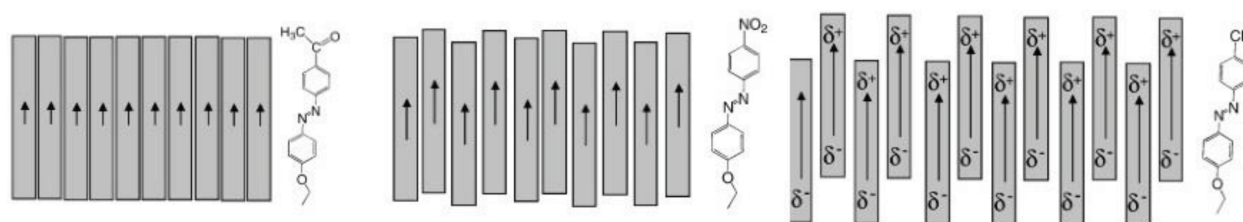


Figure 11. The representation of monolayer structure with various packing densities for azobenzene NLO compounds bearing acetyl, nitro, and cyano groups (adapted with the permission from reference [70]).

Usually, Langmuir-Blodgett films are obtained from Langmuir film deposited at the air-water interfaces with the well-known orientation of the molecule with the hydrophobic groups in air and hydrophilic ones immersed in water.

The driving forces of coherent monolayer formation are the hydrophobic interactions between the nonpolar parts and the interaction between the polar groups and the water subphase. Wang et al. [71] propose an unconventional method to prepare NLO LB films based on the molecular electrostatic interaction of hydrogen bonding in a chromophore modified with urea. The new synthesized optic active compound is 1-(10'-[(10-nitro)-6,7-azobenzen]-ether-decyl)-3-(tetracos-12,14-diynyl)urea (NAEDTDU), which exhibits an unusual packing behavior at air-water interface as it is proven by the Π -A isotherm (see **Figure 12**).

The recorded specific molecular area of NAEDTDU is $35 \text{ \AA}^2/\text{molecule}$, smaller than the molecular area of the usual urea-containing derivatives in Langmuir film ($50 \text{ \AA}^2/\text{molecule}$).

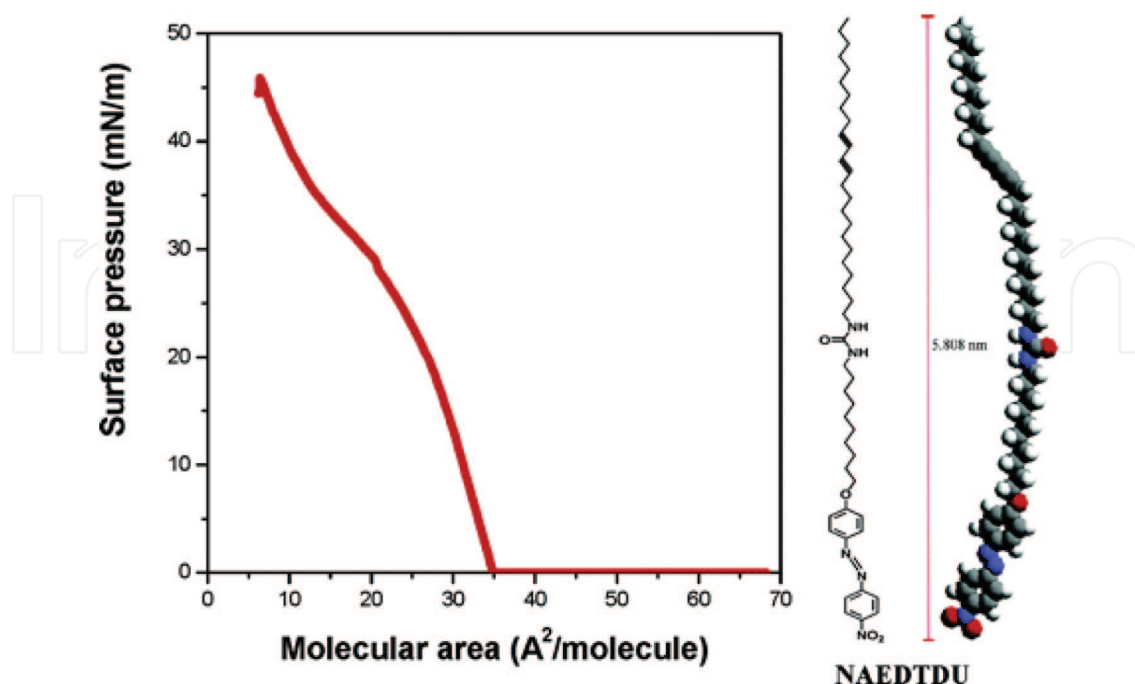


Figure 12. Π -A isotherm of Langmuir film of NAEDTDU (adapted with the permission from reference [71]).

When assuming a traditional orientation of NAEDTDU molecule in the monolayer, with the urea polar group in the water subphase and both hydrophobic alkyl chain and nitro-azobenzene group in air, the molecular modeling suggests specific surface area larger than $50 \text{ \AA}^2/\text{molecule}$. To obtain the observed $35 \text{ \AA}^2/\text{molecule}$ value, it is presumable that the nitro group of chromophore molecule lies on the air-water interface. Langmuir NAEDTDU monolayer can be transferred onto a hydrophobically modified quartz and silicon substrates using conventional vertical upward dipping technique and produces Langmuir-Blodgett multilayers. In this nontraditional LB monolayer, a peculiar aggregation of the chromophore molecules is suggested, i.e., the formation of a stable and linear network based on the hydrogen bonding between the urea groups.

The noncentrosymmetric arrangement of the NAEDTDU molecule in LB films generates relatively large intensities of SHG signal recorded. The thermal stability of SHG activity of LB multilayers was improved after photopolymerization of diacetylene moieties in film, due to the restriction of the movement of the chromophores and stabilization of their ordered orientation.

4.2. Layer-by-layer deposited thin films

The layer-by-layer (LbL) method to produce thin films is a versatile and convenient technique for the fabrication of thin films, based on the electrostatic attraction between the materials in different layers successively deposited. The most relevant advantage of LbL technique is represented by the precise control of the composition and thickness of the final film, which can be easily tuned from the chemical structure of the polyelectrolytes and deposition parameters. Acentric supramolecular architecture, as essential requirement for preservation of NLO properties, is a challenge to be achieved from chromophores and polyelectrolytes in LbL film technique. The conventional LbL technique should be adjusted in order to ensure the density and stability of the optic active molecules in the obtained film, with particular attention to be paid to the orientation of chromophore [72].

Facile fabrication of a second-order nonlinear optical films with superior properties and stability was reported [73] using a surface sol-gel synthesis of ZrO_2 layers and subsequent layer-by-layer (LbL) deposition of the nonlinear optical (NLO)-active azobenzene-containing polyanion and poly(diallyldimethylammonium chloride). The resulted material is an organic/inorganic hybrid multilayer film with noncentrosymmetrically orientated azobenzene chromophores. The specific orientation of the NLO-active azobenzene chromophores is produced by the strong repulsive interactions between the negatively charged ZrO_2 and the sulfonate groups of the sulfonate-modified azobenzene chromophore.

The SHG signal could be increased by increasing the number of deposition cycles and also with the increase of the azobenzene graft ratio in the polyion. Wang et al. [74] proposed a method to fabricate an organic/inorganic hybrid NLO film by electric field-induced layer-by-layer deposition technique. The compound used to produce alternative layers is a new synthesized polycation from aromatic diazo group linked silicon and a chromophore molecule 2-([4-[4-(2-carboxy-2-cyano-vinyl)-phenylazo]-phenyl]-methyl-amino)-ethyl acid (DRCB) as anion.

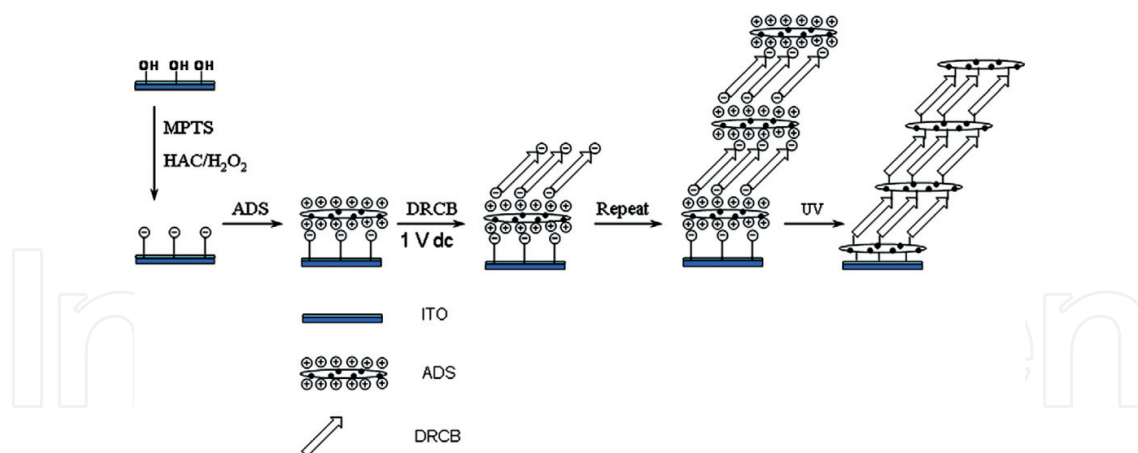


Figure 13. The structure of the ADS-DRBC hybrid thin film (adapted with the permission from reference [74]).

Using electric field in assembling process, the oriented adsorption of chromophores is facilitated, and the density of oriented optic active molecules increases. The preparation of the hybrid film using LbL deposition of aromatic diazonium salt-linked silicon sol (ADS) and DRCB chromophore on ITO glass previously functionalized with (3-mercaptopropyl)-trimethoxysilane (MTPS) is presented in **Figure 13**.

The UV irradiation of deposited multilayered films results in transformation of the electrostatic interaction between layers in covalent bonds, leading to a significant increase of the thermal and chemical stability of the final material. The architecture assembles with the aid of the electric field ensuring a high degree of molecular orientation of chromophores; thus, large second-harmonic generation signal of the LbL film was observed.

5. Theoretical modeling

In order to rational design the host-guest material, molecular dynamic simulation is used for quantum chemical calculation. The structures of considered molecules are simulated by using molecular dynamics, and relevant electrical properties, such as polarizability α and β , could be computed with density functional theory (DFT). For example, Makowska-Janusik (3) reports the investigation of the influence of polymeric matrix on the NLO properties of the pyrazoloquinoline derivatives in poly(methyl methacrylate) matrix. According to the chemical structure of the chromophore molecules, the best description of the pyrazoloquinolines-PMMA systems could be obtained by using various approaches, such as point-dipole or distributed molecular response models, with good concordance with the experimental data. Molecular simulation is also performed in order to elucidate the origin of the NLO behavior in composite materials, since in experimental approach it is not possible to separate the contributions of each component. The molecular modeling methods can provide explanations about the nature of the guest-host interaction based on the separate different contribution of the components to the optical properties.

A particular kind of host-guest material exhibiting NLO properties is obtained by using semiconducting nanoparticles (quantum dots) as optical active materials. The interface phenomena play an important role in tuning the NLO properties of these materials.

An innovative approach is reported by Britton et al. [75], to significantly increase the nonlinear properties when combining in the polymeric matrix a low symmetry phthalocyanine derivative with CdSe/CdS quantum dots. The new synthesized metal-free chromophore 2,3-bis[2'-(2''-hydroxyethoxy)ethoxy]-9,10,16,17,23,24-hexa-*n*-butoxyphthalocyanine exhibits by itself an unusual electric properties due to the high dissymmetry of electronic density in the molecule. The addition of CdSe/CdS quantum dots to the phthalocyanine in chloroform solution produces a negligible effect on the values of the imaginary component of the third-order optical susceptibility and nonlinear absorption coefficient β_{eff} . However, when the dye is embedded into a polycarbonate matrix, a twofold increase of the abovementioned optical properties is recorded, while the incorporation of both phthalocyanine and CdSe quantum dots into the polymeric film produces a three-times increase of the third-order optical susceptibility compared to the chloroform solution of the dye. The chromophore molecules and CdSe/CdS nanoparticles are in close proximity when they are locked together in the polymeric film; thus, the heavy atom effect could manifest, resulting in a significant improvement of NLO properties.

6. Conclusion

The synthesis of the most important classes of the organic compounds, alkyne, dye, heterocycle, thienyl, and ferrocene compounds, was presented. A lot of important reactions, like Sonogashira, Suzuki, Heck, Huisgen, Wadsworth-Emmons, Vilsmeier-Haack-Arnold, Wittig, etc., were employed for the synthesis of the new compounds with nonlinear optical applications. The synthesis of the new molecules possessing privileged structures, with a couple donor-acceptor or “push-pull” molecules, was the purpose of the last decades. Besides, new unorthodox structures, which do not possess this system, but with very good NLO properties and very good SHG signal, were reported, and the number of these increase every year. The most important parameters in the characterization of the new NLO organic compounds are the HOMO-LUMO energy gap and the first-order hyperpolarizability β_{tot} . Small energy gaps and high hyperpolarizabilities define the best compounds with nonlinear optical applications.

Thin films were fabricated by incorporating substances with NLO properties in a large variety of polymers to improve the performance of the resulted hybrid system. Polymethyl methacrylate is the most used polymer, but silica matrix is preferred. Also, Disperse Red 1 in a silica glass allows uniform dispersion and arrangement of the chromophore molecules in the cross-linked polymeric matrix. The new hybrid films are fabricated by sol-gel synthesis. The morphology of the silica matrix is very important for a good NLO behavior. Each class of organic compounds possesses a specific method for the fabrication of the thin films in order to increase their NLO properties. Thus, azo-photosensitives dyes are encapsulated. Noncentrosymmetric arrangement for the dipolar push-pull chromophores embedded in a polymeric matrix is

obtained when heating the system to the glass transition temperature (T_g) of the polymer. Langmuir-Blodgett films, which exhibit better NLO properties, are obtained from Langmuir film deposited at the air-water interfaces with the well-known orientation of the molecule with the hydrophobic groups in air and hydrophilic ones immersed in water. A convenient technique for the fabrication of thin films is the layer-by-layer (LbL) method which presents the advantage of the precise control of the composition and thickness of the final film. Both theoretical modeling and experimental approach should be addressed, in order to find the best matching between the host and guest material. In addition, the influence of the surface and film formation method should be considered, with a particular attention to the thermo- or photosensitive chromophores.

Conflict of interest

The authors have no conflict of interest to declare.

List of abbreviations

SHG	Second-harmonic generation
HOMO-LUMO gap	The difference between the energy of the highest occupied molecular orbital and the lowest unoccupied molecular orbital (eV)
α	Molecular polarizability (esu·D)
β_{tot}	First-order hyperpolarizability (esu·D)
μ_{tot}	Dipole moment (D)
Q	Quadrupole moment (D)
T_g	Glass transition temperature (°C)
LbL	Layer-by-layer deposition technique

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